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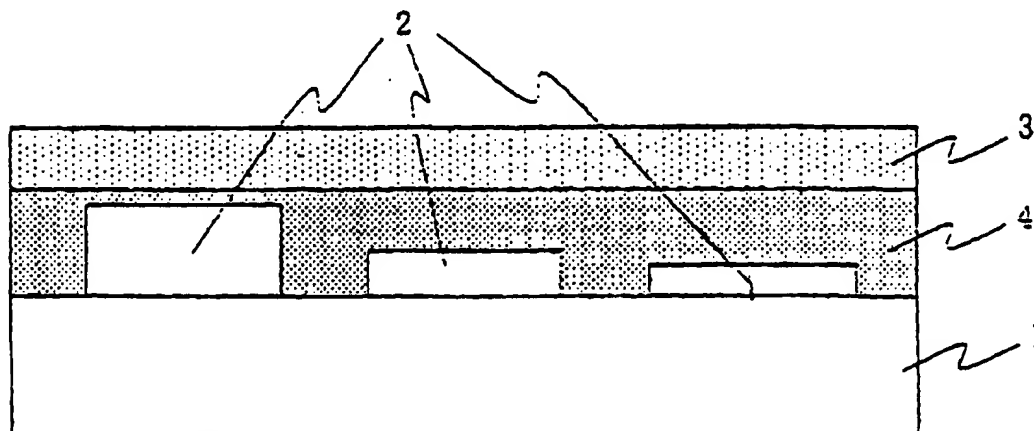
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(54) Abstract Title

Colour filter

(57) A colour filter comprising a transparent substrate 1, patterned colour layers 2, a transparent electrode 3 and a flat transparent protection layer 4. The flat transparent protection layer 4 covers both the transparent substrate 1 and the patterned colour layers 2. The flat transparent protection layer 4 comprises a UV or light radiation and/or heat cross-linkable polymerisation product of a mixture containing (a) a polymerisation component comprising monomers, oligomers or polymers, having hydroxyl, carboxyl or amino groups and (b) a metal containing compound. An Example of a metal containing compound is an alkoxide, phenoxide, acylate or chelate of a metal atom, such as Al, Zr, Si, In, Zn, Ni, Ti, Cu, having 1-18 carbon atoms. The mixture is deposited by a wet method such as spin, roll or cast coating. The colour filter is suitable for use in an organic polychromatic-light emitting display device.

Figure 2



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Figure 4

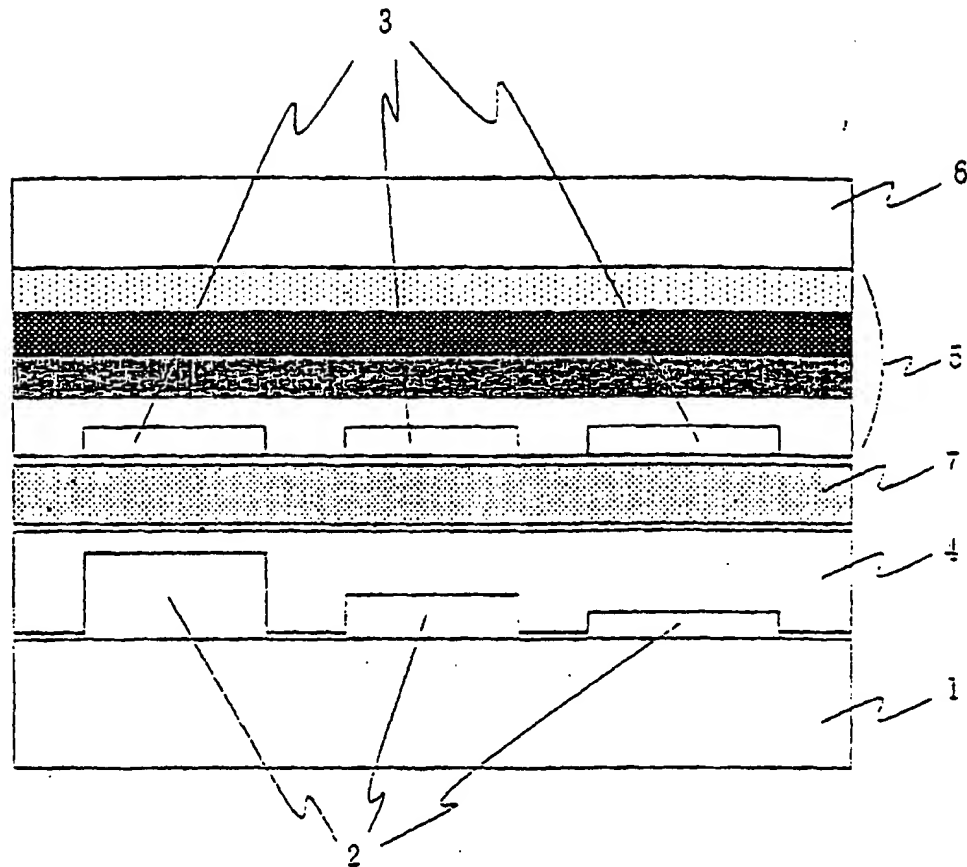
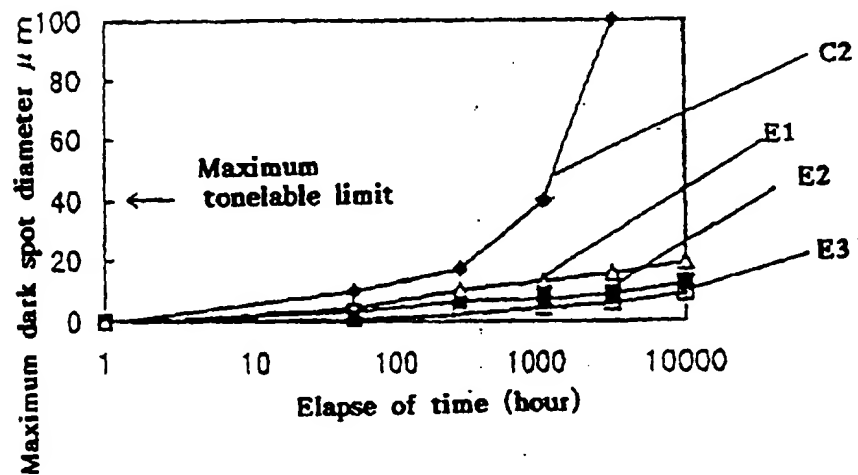


Figure 5



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Figure 1

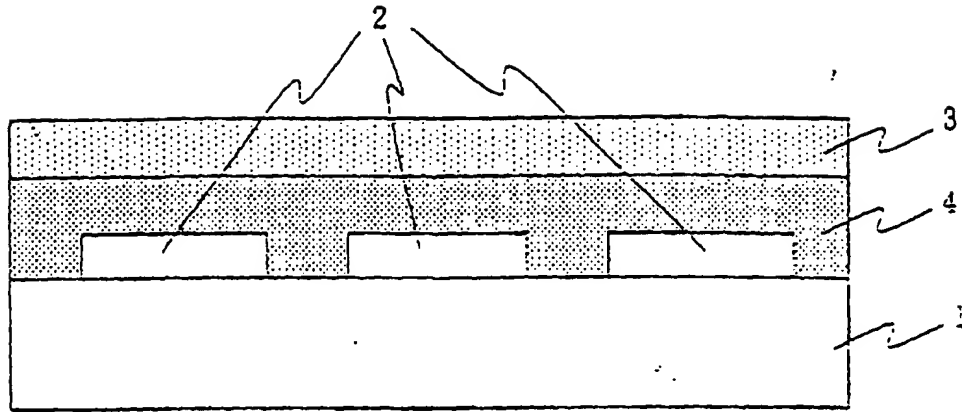


Figure 2

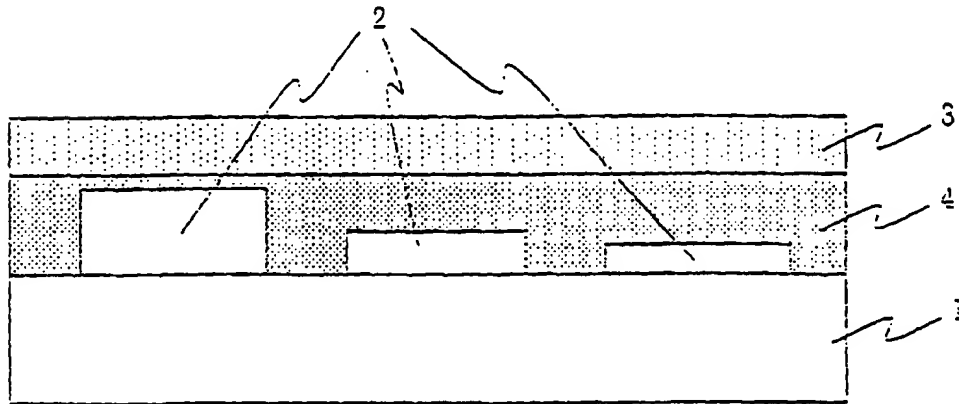


Figure 3

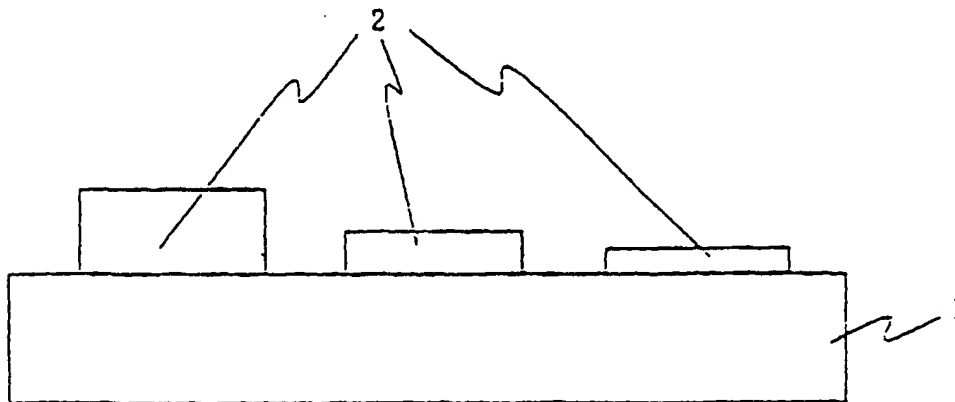


Figure 6

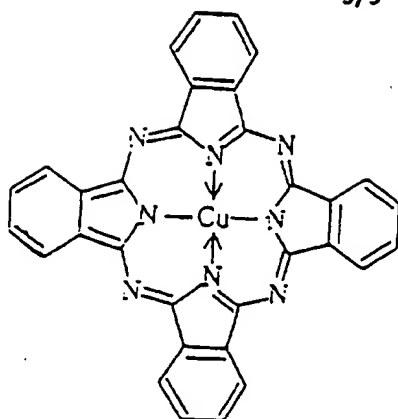


Figure 7

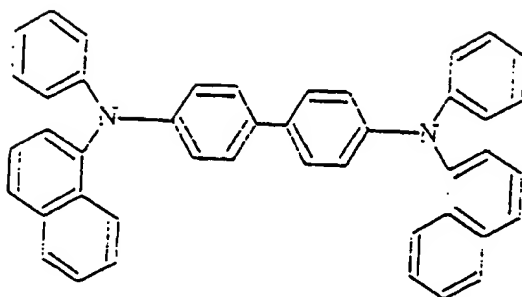


Figure 8

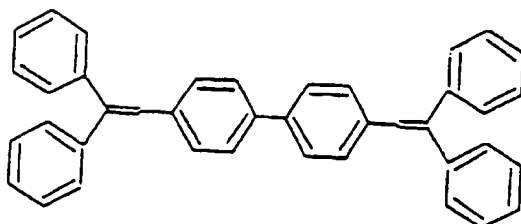
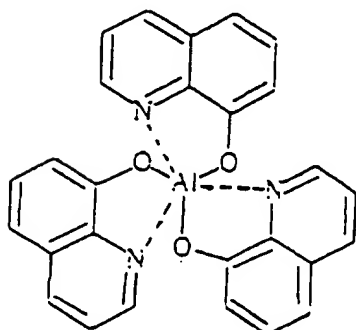


Figure 9



## COLOUR FILTER AND ORGANIC POLYCHROMATIC-LIGHT EMITTING DISPLAY DEVICE INCLUDING THE SAME

The present invention relates to a high-definition colour filter that facilitates displaying multiple colours and exhibits excellent environmental resistance and excellent productivity. The present invention also relates to an organic polychromatic-light emitting display device including such an excellent colour filter. Specifically, the present invention relates to a colour filter and an organic polychromatic-light emitting display device, including the colour filter, and used for display purpose in image sensors, personal computers, word processors, TV sets, facsimiles, audio sets, video players, car navigation sets, desktop computers, telephone sets, portable terminals and various industrial instruments.

It has been required for the display devices, including the solid state image pick-up tube, used in processing increasing and diversifying data to be beautiful in shape, light in weight, slim in volume and excellent in performance. Research and development for low power consumption and high response speed of the display devices have been explored vigorously. Especially, various efforts have been focused on the display device that facilitates displaying full colours with high definition.

The colour filter as shown in Fig 1 is indispensable to provide the colour image elements in the solid state image pick-ups and the liquid crystal display devices developed in early eighties with full colour display function. This colour filter includes a substrate 1, patterned colour resolution layers 2 on the substrate 1, a protection layer 4 covering the patterned colour resolution layers 2 and the substrate 1, and a transparent electrode 3 on the protection layer 4. Hereinafter, the patterned colour resolution layer will be referred to as the "colour resolution layer".

It is required for the colour filter to exhibit various properties such as 1) high definition, high transparency and high contrast of the colour dots; 2) high optical density and high definition of the

black matrix; 3) durability and flatness; 4) chemical resistance and thermal resistance against the subsequent manufacturing step; and 5) mass-productivity.

The dyeing method, pigment dispersion method and printing method are used for manufacturing the colour filter. The dyeing method is effective to realize high colour definition and high transparency, since the dyeing method dyes the resist stuff, represented by gelatin, in the solution containing a dye for a specific wavelength. However, the dyeing method is not so effective to realize light resistance, thermal resistance, chemical resistance and moisture resistance. The pigment dispersion method disperses the pigments such as the phthalocyanine pigments (blue and green) and the anthraquinone pigments (red) with average particle diameter of  $0.1\ \mu\text{m}$  or less in the resist stuff, represented by acrylic resin and patterns the colour resist. The pigment dispersion method is superior to the dyeing method in the resistance items but inferior to the dyeing method in the optical transparency. It is necessary for the pigment dispersion method to include additional steps, since an oxygen interruption film is used in the light exposure process. The pigment dispersion method is not so good at fine patterning. The printing method is simple and convenient. However, it is difficult for the printing method to realize excellent surface properties, colours with high definition and fine patterning.

It is required for the protection layer (protection film), that protect the line pattern of the colour resolution layers formed by one of the foregoing methods, to exhibit the following chemical, optical and mechanical properties.

- (1) No influence (bleaching, colour tone change, etc.) to the colouring stuffs (dyes, pigments).
- (2) No pattern distortion.
- (3) Excellent adhesion to the colour resolution layers and the substrate. Excellent adhesion to the layers, including the transparent electrode, formed in the subsequent process.
- (4) High transparency (No absorption in the visible region).
- (5) Excellent thermal resistance, excellent chemical resistance and excellent water resistance.
- (6) Excellent smoothness and high hardness of the surface.

(7) Endurance against the subsequent steps for forming the transparent electrode and such layers.

The following materials have been proposed for the protection layer of the liquid crystal and such optical modulation elements.

Various coating agents, which maintain shape of the line pattern, hardly affect chemically to the pigments, insulate the substrate, flatten the substrate and prevent physical and mechanical break down of the light emitting element from causing, have been proposed for the materials of the protection layer. The proposed coating agents include acrylic resins (cf. Japanese Unexamined Laid Open Patent Application No. S60-216307), epoxy resins (cf. Japanese Unexamined Laid Open Patent Application No. H04-97102 and Japanese Examined Patent Application No. H03-8652), polyimide resins (cf. Japanese Unexamined Laid Open Patent Application No. H01-229203) and silicone resins (cf. Japanese Unexamined Laid Open Patent Applications No. H06-19216, H08-279394 and No. H09-49902).

However, it is necessary to irradiate ultraviolet light to the foregoing coating agents or to thermally treat the foregoing coating agents at 200°C or higher. Therefore, it is very difficult for the foregoing coating agents to form the protection layer, that maintains the high definition of the pattern of the under layers, flattens the under layers while maintaining the steps in the edge portions and endures the subsequent manufacturing steps without deteriorating the pigments in the underlying colour resolution layers. Any protection layer, that meets the above described requirements and is manufactured with excellent mass-productivity, has not been realized yet.

The colour filter and its protection layer for the liquid crystal display device have been described so far. In the late eighties, Tang et al. reported a laminate-type organic electroluminescent device (hereinafter referred to as an "organic EL device") that has a laminate structure of organic molecule thin films and facilitates obtaining high luminance of 1000 cd/m<sup>2</sup> or more at an applied voltage of 10 V (Tang et al. Appl. Phys. Lett., 51, (1987) 913). The organic EL device is featured by a wide angle of visibility and high response speed. Since then, research and development of the organic EL device have been explored vigorously. Research and development of the similar device that employs organic polymers have been also explored vigorously. In association with this,

research and development of the colour filter for the organic EL devices have been explored vigorously.

Since the organic EL device facilitates obtaining a high current density at a low applied voltage, the organic EL device is expected to emit light at higher luminance and at a higher efficiency than those of the inorganic EL device and the LED. The organic EL device is of self-light-emission type. Therefore, the organic EL device is expected to have excellent features such as high luminance, high contrast, high light emission efficiency at a low drive voltage, high definition, wide angle of visibility, high response speed, fine pixels, polychromatic display capability, light weight, and thin thickness. Due to these specific features, the organic EL device is expected to be applicable to the flat panel display, that is beautiful, light in weight, slim in volume and excellent in performance.

The organic EL device has a laminate structure including organic polymer layers laminated on a transparent electrode. Typical laminate structure are described below.

- (1) Anode (transparent electrode)/Organic light emitting layer/Cathode (electrode)
- (2) Anode (transparent electrode)/Hole injection layer/Organic light emitting layer/Cathode (electrode)
- (3) Anode (transparent electrode)/Organic light emitting layer/Electron injection layer/Cathode (electrode)
- (4) Anode (transparent electrode)/Hole injection layer/Organic light emitting layer/Electron injection layer/Cathode (electrode)

These laminate structures are formed by the methods disclosed in the publications of the following Japanese Unexamined Patent

Applications: H05-21163, H05-114487, H05-94876, H05-94877, H05-125360, H05-134430, H06-200242, H06-234969, H07-11245, H07-11246, H07-142168, H07-282975, H08-213171, H08-227276, H08-236273, H08-279394, H08-302340, H08-315981, H09-022782, H09-102393, H09-153395, H09-204983, H09-204984, H09-204985, H09-209127, H09-232075, H09-272864, H09-283279, H09-293589, H09-298090, H09-306666, H09-306668, H09-330791, H09-330792, H10-012378, H10-012379, H10-012380, H10-012383, H10-022072, H10-022076, H10-039792, H10-069981, H10-083889, H10-092583, H10-106746, H10-106753, H10-125471, H10-125472, and H10-125473.



The requirements to the organic EL device will be described below.

- (1) It is necessary to inject carriers from outside, since the organic EL device includes inorganic insulators which does not have carriers in it.
- (2) It is necessary to improve the transport efficiencies and the recombination probability of the injected hole and electrons.
- (3) It is necessary for the organic thin film materials to be stable enough thermally, physically and chemically to prevent the organic thin films from deterioration by heat, moisture and hazardous gases and to realize flat and smooth boundaries and surfaces of the formed organic thin films.
- (4) It is necessary to realize excellent colour balance between the emitted polychromatic rays, high luminance and high light emission efficiency.

An on-vehicle monochromatic green organic EL display has been put into market by Tohoku Pioneer Electronic Corp. since December, 1997. To meet the diversifying market needs, it is necessary to quickly develop organic EL display devices for displaying polychromatic or full-colour images with a high response speed and with high definition. Especially, capability of displaying colours with high definition is indispensable for the high-performance display devices (cf. "Kinou Zairyou (Functional Materials)" (in Japanese), vol. 18, No. 2, p96.).

The organic EL devices proposed so far for displaying polychromatic images will be described below.

- (1) An organic EL device that includes organic EL layers for the three primary colours patterned one by one such that organic EL elements (pixels) for the three primary colours are arranged on a plane in a predetermined pattern.
- (2) An organic EL device that includes an organic white light emitting element and colour filters combined with the organic white light emitting element for obtaining the three primary colours (red, green and blue).
- (3) An organic EL device that includes an organic blue light emitting element and colour conversion filters, combined with the organic blue light emitting element, which convert the blue light to the fluorescent

light of longer wavelengths (green and red) so that the light of the three primary colours may be obtained. (cf. Japanese Unexamined Laid Open Patent Applications No. H03-152897 and No. H05-258860).

(4) An organic EL device that employs the micro-cavity system.

(5) An organic EL device that includes a laminate of a red-light emitting layer, a green-light emitting layer and a blue-light, emitting layer.

(6) An organic EL device that employs the voltage control method.

As for the organic EL device (1), since the organic EL layers are patterned one by one by photolithography to arrange the organic EL elements (pixels) for the three primary colours on a plane, the efficiencies of the elements lowers greatly due to the repeated exposure in the development process. It is difficult to manufacture the organic EL device (1) with reasonable mass-productivity due to the complicated manufacturing steps. The materials which emit the light of the respective three primary colours with high efficiencies have not been obtained yet. Especially, the efficiency of red light emission is low. Due to the reasons described above, the organic EL device (1) has not been developed yet. The process for manufacturing the organic EL device (4) is complicated. Although the organic EL device (5) is an ideal one from the stand point of display quality and effective use of the display area, it is difficult to realize a high-definition pattern and a practical driving method. As for the organic EL device (6), many problems are left unsolved in the colour range changeable by voltage application and the gradation display. In view of the foregoing, the organic EL devices (2) and (3) according to the colour filter method may be practical and easy to develop. However, the organic EL device (2) is not so advantageous from the view point of light emission efficiency, since the efficiency at that the organic EL device (2) emits one of the three primary colours is limited to one third of the total efficiency. Moreover, any organic light emitting element, that emits white light at sufficient luminance, has not been obtained yet. The colour filter similar to those used in the liquid crystal display devices may be employable to the organic EL device (2). However, any practical protection layer, that endures the subsequent manufacturing steps and is excellent optically, physically, chemically and mechanically, has not been realized yet.

The light emitting element for the organic EL device (3) is not limited to the one that emits white light. Light emitting elements which emit light at higher luminance may be used for the organic EL device (3). Especially, the efficiency of the colour conversion, that converts the blue light from a blue-light emitting element to the light at a longer wavelength, exceeds 60%: most efficient in principle. The colour filter used for this colour conversion scheme has a structure as shown in Figure 2. Referring now to Figure 2, the colour filter includes patterned colour conversion layers 2 on a substrate 1, a protection layer 4 covering the patterned colour conversion layers 2 and the substrate 1, and a transparent electrode 3 on the protection layer 4. Hereinafter, the patterned colour conversion layer will be referred to as the "colour conversion layer".

Japanese Unexamined Laid Open Patent Applications No. H03-152897 and No. H05-258860 disclose a colour conversion method that uses the fluorescent pigments, which absorb the light from an organic EL element and emit fluorescent light in the visible region, in the colour filter for converting the blue light to the fluorescent light at longer wavelengths (green and red) such that the three primary colours are obtained. The light emission efficiency of the colour conversion method that uses fluorescent layers is determined by the product of the absorption efficiency and the fluorescent efficiency of the fluorescent material. The colour conversion method is advantageous for emitting light in the three primary colours with a high conversion efficiency by using fluorescent materials, the absorption efficiency and the fluorescent efficiency of which are high. Due to the reasons described above, the method that displays the three primary colours utilizing colour conversion by fluorescent layers is the most advantageous and most hopeful one for practical use.

The problems of the organic EL device (3) that uses a colour conversion filter include the problems of the organic EL element, development of colour conversion pigments with a high colour conversion efficiency, the chemical, mechanical and physical resistance of the colour conversion pigments, and development of the colour filter that facilitates its fine patterning and exhibits excellent resistance against the subsequent manufacturing steps of the organic EL device.

More in detail, the distance between the colour conversion filter and the organic EL element poses a serious problem to the performances of the polychromatic light emitting display devices. As the distance is longer, the light from a pixel tends to leak more to the adjacent pixels, causing a narrow angle of visibility. To describe in other words, as the distance between the colour conversion filter and the organic EL element is shorter, the angle of visibility is wider. Therefore, it is desirable in principle to form a transparent electrode and an organic EL element directly onto the upper surfaces of the colour conversion layers.

The colour conversion pigments, used in the colour conversion filter for converting the light emitted from the organic EL element to the light of the intended wavelengths, is not resistant against the light of a specific wavelength, moisture, heat and organic solvents. The colour conversion pigments are deactivated easily by the light of the specific wavelength, moisture, heat and organic solvents. Therefore, the structure of the polychromatic-light emitting display device and the method of manufacturing its colour conversion filter subject to various limitations.

For the colour conversion pigments used in the colour conversion filter, the fluorescent pigments such as the Rhodamine pigments, pyridine pigments, oxazine pigments, coumarin pigments and cyanine pigments are used. These fluorescent pigments are disclosed in Japanese Unexamined Laid Open Patent Applications No. H08-78158, No. H08-222369, No. H08-286033, No. H09-106888, No. H09-208944, No. H09-245511, No. H09-330793, and H10-12379.

As described above, it is known that light, heat or organic solvents adversely affect the fluorescent pigments and cause fluorescent wavelength change and extinction. Radicals and ions produced from the optical reaction initiator and the reactive monomers cause bleaching of the fluorescent pigments and extinction (cf. Japanese Laid Open Patent Application No. H07-268010). Therefore, in forming the transparent electrode and the light emitting layer of the organic EL element directly onto the upper surfaces of the colour conversion layers, the functions of the colour conversion layers are lost easily by the heat and plasma produced in the sputtering process of the transparent electrode or by the separating liquid used in patterning the transparent electrode.

Highly transparent resins, such as the matrix resins disclosed in the Japanese Laid Open Patent Application No. H08-222369, which are not influential chemically to the foregoing pigments are preferable as the matrix material of the colour conversion layers. In addition, the poly(vinyl alcohol) resins, polyacrylate resins, polyimide resins, epoxy resins, and polyurethane resins, which are used for the liquid crystal display, are used as the matrix resin of the colour conversion layers. For example, the resist materials, which have reactive vinyl groups, such as the acrylic resins, the methacrylic resins, the polycinnamate resins and the cyclic gums are used as the photosensitive resin, so that the photolithographic process is applicable. In the similar manner as in the case of inorganic pigments, the liquid resist (photosensitive polymer) into which the fluorescent pigment is dispersed and dissolved is coated by spin-coating (cf. Japanese Laid Open Patent Applications No. H05-198921 and No. H05-258860), roll-coating and printing, which are expected to be easily applicable to the manufacture of the above described colour filter. The coated resin layer is patterned by the printing method or by the photolithographic method. The photolithographic method is especially preferable to form a pattern with high definition.

The colour conversion layers are different in thickness from each other, depending on the conversion characteristics (efficiency and colour tone) of the fluorescent pigments for the respective colours, to obtain the desired colour tones. The thickness differences between the colour conversion layers cause steps between the colour conversion layers 2 on the transparent substrate 1 as shown in Figure 3. When the transparent electrode 3 and the organic EL element are formed directly onto the steps, an open circuit of the electrode is caused, the colour conversion pigments are damaged, the layer pattern is deformed, optical thickness deviations are caused across the organic light emitting layer, the function of the colour filter is impaired and stable light emission is not obtained from the organic light emitting layer. And, the resulting display device fails to emit polychromatic light with high definition.

In view of the foregoing, it is not practical to form the transparent electrode 3 directly onto the colour conversion layers 2. It is necessary to interpose a protection layer 4 between the colour conversion layers 2 and the transparent electrode 3. Interposition of the

protection layer is important to develop a polychromatic-light emitting display device that is excellent in light emission, angle of visibility, colour reproducibility, storage stability, and driving stability.

The protection layer is required to exhibit the following properties, considering the limitations against light, heat and solvents of the colour conversion pigments and the existence of the steps between the colour conversion layers, in addition to the requirements to the protection layer of the colour filter for the liquid crystal display device.

The protection layer is required (i) not to erode the pattern of the colour conversion layers nor to deactivate the fluorescent pigments in the colour conversion layers; (ii) to be thick enough to bury the steps between the colour conversion layers but thin enough (as thin as several  $\mu\text{m}$ ) to maintain a wide angle of visibility; (iii) to be highly transparent optically; (iv) to be resistant against heat; (v) to be very flat and smooth, causing no protrusions on the surface; (vi) to be very adhesive to the colour conversion layers and the substrate; (vii) to be excellent in the resistance against chemical reagents; (viii) to be excellent in moisture-proof; (ix) not to cause evaporation of the residual monomers and solvents; (x) to be mechanically strong to some extent; (xi) to cause no protrusions of the foreign substances, and (xii) to be endurable against subsequent manufacturing steps. The protection layer that meets the above described requirements is transparent enough to effectively transmit the light from the organic EL layer to the colour conversion layers causing neither attenuation nor scattering. The protection layer flattens the thickness differences (concave and convex portions) between the colour conversion layers. The protection layer protects the colour conversion layers against external optical factors, chemical factors such as reagents and solvents, and physical and mechanical factors such as impact and stress exerted during film lamination. The protection layer facilitates realizing a polychromatic-light emitting display device without adversely affecting the colour conversion performance and the life and stability of the organic EL element.

Although various materials and methods of forming have been proposed so far for the protection layer, any protection layer that meets all the foregoing requirements has not been realized yet, posing serious

problems to providing the organic EL devices with polychromatic or full-colour display capabilities.

The methods for forming the protection layer may be classified into the dry method such as sputtering, vacuum deposition and plasma deposition and the wet method such as spin-coating, roll-coating and cast-coating. The dry method is useful to form the film of inorganic materials such as silica, alumina and titanium oxide (cf. Japanese Unexamined Laid Open Patent Application No. H07-104114) and organic materials such as parylene and polyamide. However, the dry method has some problems in protecting the pigments in the colour conversion layers against thermal influences, in uniformly burying and flattening the steps between the colour conversion layers, and in productivity.

Various investigations have been made on forming the protection layer by the wet method. The materials used for forming the protection layer includes the materials described above, photo-curing resins, thermosetting resins and photo- and thermo-setting resins such as silicone resins modified with imide (cf. Japanese Unexamined Laid Open Patent Applications No. H05-134112, No. H07-218717 and No. H07-306311); acrylic resins, polyimide resins and silicone resins into which an inorganic metal compound such as  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  is dispersed (cf. Japanese Unexamined Laid Open Patent Applications No. H05-119306 and No. H07-104114); acrylate resins modified with epoxy as an ultraviolet-ray curing resin (cf. Japanese Unexamined Laid Open Patent Application No. H07-48424); resins and resist resins polymerized from acrylate monomers, oligomers and polymers having reactive vinyl groups (cf. Japanese Unexamined Laid Open Patent Applications No. H06-300910, H07-128519, H08-279394 and No. H09-330793); inorganic compounds for the sol-gel method (cf. Monthly DISPLAY, Vol. 3, No. 7 (1997) and Japanese Unexamined Laid Open Patent Application No. H08-27934); and fluororesins (cf. Japanese Unexamined Laid Open Patent Applications No. H05-36475 and H09-330793). The Japanese Unexamined Laid Open Patent Application No. H08-279394 discloses a protection structure that includes an insulative inorganic oxide film on the upper surfaces of colour conversion layers and a conventional organic polymer protection layer on the insulative inorganic oxide film. However, the formation of the insulative inorganic oxide film on the upper surfaces of colour conversion layers damages the pigments by

thermal shock and exerts mechanical stress to the colour conversion layers, causing pattern deformation of the colour conversion layers. In addition, the subsequent formation of the protection layer on the insulative inorganic oxide film exerts heat and light to the colour conversion layers, further damaging the pigments in the colour conversion layers. Thus, the formation of the insulative inorganic oxide film on the upper surfaces of colour conversion layers poses many problems to the manufacturing process.

The modified resins such as acrylate resins, methacrylate resins and epoxy resins are representative photo-curing resins, thermosetting resins or photo- and thermo-setting resins used for the protection layers of the colour filters in the conventional liquid crystal display devices and image scanners. The modified resins cause deactivation and such adverse effects of the colour conversion pigments due to their reactive polar vinyl groups and due to the radicals and ions produced from the polymerization initiator. More in detail, the pigment used is dimerized and its  $\pi$  conjugate bondings are disconnected by the irradiation of light, especially by the irradiation of strong ultraviolet light. As a result, the pigment is prevented from converting the light form the light emitting element to the fluorescent light originally intended. Therefore, when a photo-curing resin, especially an ultraviolet light curing resin, is used in the protection layer for protecting the colour conversion film, the components, reaction mechanism and light intensity should be considered carefully so as not to adversely affect the fluorescent materials (colour conversion pigments).

When the resin, represented by polyimide, that hardens at a high temperature of 200°C or higher is used for the protection layer, the colour conversion characteristics are deteriorated by heat depending on the combination of the fluorescent pigments and the matrix material of the colour conversion layers. To maintain the colour conversion characteristics, it is desirable to form the protection layer at a temperature lower than 200°C. The use of polyimide and such resins which harden at 200°C or higher poses serious problems.

Since the fluorescent pigments are dissolved by the monomer components of the photo-curing resin or the thermosetting resin and by the



solvent, causing definition lowering, colour conversion efficiency lowering and such adverse effects.

A typical coating method for coating the colour filter is the sol-gel method (cf. Monthly DISPLAY, Vol. 3, No. 7 (1997), p119). The inorganic (straight silicone resin) coating layer, formed by cross-linking the straight silicone resin with -Si-O-Si- bondings by the sol-gel method, exhibits many merits such as excellent thermal resistance, excellent weather proof, excellent resistance against solvent and high hardness. Especially, this inorganic resin coating layer is superior to the ordinary organic resin coating layers in thermal resistance. The straight silicone resin exhibits less decomposition and deterioration such as discoloration and choking than the organic coating resin does. The straight silicone resin also exhibits excellent water repellence, excellent moisture resistance and excellent water resistance. The straight silicone resin contains the -Si-O-Si- bonding as its main chain and the methyl group and such alkyl groups and the phenyl group and such aromatic groups in its side chains in the same manner as the other silicone products. The straight silicone resin is advantageous to obtain a very hard coating film, since the straight silicone resin has a three-dimensional cross-linking structure with a very high cross-linking density, once it is hardened. However, since the thickness of the film formed by the sol-gel method is in the order of sub-microns, that is not thick enough to bury the steps between the colour conversion layers, any uniform and flat protection layer of the straight silicone resin is not formed by the sol-gel method on the colour conversion layers. The thick film formed from the coating liquid with increased viscosity or by repeated coating is not strong enough against stress deformation, and cracks and such breakdown are caused, adversely affecting the patterns of the colour conversion layers. The straight silicone resin layer formed by the sol-gel method is completely hardened at 240°C or higher. Such a high temperature deactivates the fluorescent materials.

As described above, there exist many limitations in forming a protection layer on the colour conversion layers. The protection layer of the colour filter must not deteriorate the fluorescent materials. The protection layer must not include any foreign substances, surface defects or protrusions. The foreign substances, surface defects and protrusions

cause display defects called "dark spots". The material and structure for the protection layer which neither deteriorate the fluorescent pigment nor cause display defects have not been found yet.

In view of the foregoing, it is an object of the invention to provide a protection layer for the colour filter used in display devices, image sensors and high-performance polychromatic-light emitting devices. It is another object of the invention to provide a colour filter including a protection layer that is excellent in transparency, adhesiveness, thermal resistance, water proof, chemical resistance, hardness, flatness, and resistance against subsequent manufacturing steps, and that does not adversely affect the colour conversion layers. It is still another object of the invention to provide a polychromatic-light emitting display device that includes such a colour filter.

The present inventors conducted intensive studies on the protection layer of the colour filter that does not adversely affect the conversion characteristics of the colour filter, and the stability and life of the organic EL element. The present inventors have found that the foregoing objects are achieved by using a polymerization product of a specific polymerizing compound and a specific metal compound.

According to an aspect of the invention, there is provided a colour filter including: a transparent substrate; patterned colour layers on the transparent substrate, each of the patterned colour layers being formed by patterning a resin film containing a pigment; a transparent and flat protection layer covering the transparent substrate and the patterned colour layers; and a transparent electrode on the protection layer; the protection layer including a cross-linking polymerization product of a mixture containing a polymerizing component (a) and a metal-containing compound (b), the mixture being deposited by the wet method such that a layer of the mixture is formed, the cross-linking polymerization using radiation, heat, or radiation and heat; the polymerizing component (a) containing monomers, oligomers or polymers capable of being polymerized by radiation, heat, or radiation and heat; the monomers, oligomers and polymers having hydroxyl groups, carboxyl groups or amino groups; the metal-containing compound (b) being metal alkoxide, metal phenoxide, metal acylate or metal chelate having from 1 to 18 carbon atoms.

Advantageously, the monomers, oligomers or polymers have acryloyl groups or methacryloyl groups and the metal atom is the one selected from the group consisting of Al, Zr, Si, In, Zn, Ni, Ti, and Cu.

Advantageously, the protection layer contains from 1 to 100 weight parts of the metal-containing compound (b) with respect to 100 weight parts of the monomers, oligomers or polymers.

Advantageously, the glass transition temperature of the protection layer is 140°C or higher, the thickness of the protection layer is 15  $\mu\text{m}$  or thinner, and the concave and convex portions on the surface thereof are 0.2  $\mu\text{m}$  or less in height.

Advantageously, at least one or two of the pigments exhibit a colour conversion function.

According to another aspect of the invention, there is provided an organic polychromatic-light emitting display device including the colour filter described above and an organic electroluminescent element on the colour filter, the organic electroluminescent element including an organic light emitting layer, the organic light emitting layer emitting light by carrier injection, the colour filter emitting polychromatic light in response to the light from the organic light emitting layer.

Now the present invention is explained hereinafter with reference to the accompanied drawing figures which illustrate the preferred embodiments of the invention, in which:

Figure 1 is a cross section of a colour filter, including colour resolution layers and used mainly in the liquid crystal display device, according to an embodiment of the invention;

Figure 2 is a cross section of a colour filter, including colour conversion layers and used for the colour conversion according to another embodiment of the invention;

Figure 3 is a cross section showing the substrate and the colour conversion layers of the colour filter of Figure 2;

Figure 4 is a cross section of an organic polychromatic-light emitting display device that includes a laminate of an organic EL light emitting element on the colour filter of Figure 2;

Figure 5 is a set of curves plotting the dark spot sizes in the display devices according to the embodiments of the invention and a display device according to one of the comparative examples;

Fig. 6 describes the structural formula of copper phthalocyanine (CuPc), used for the hole injection layer;

Fig. 7 describes the structural formula of 4,4'-bis[N-(1-naphthyl)-N-phenylamino]-biphenyl ( $\alpha$ -NPD), used in the hole transport layer;

Fig. 8 describes the structural formula of 4,4'-bis(2,2-diphenylvinyl)biphenyl (DPVBi), used in the light emitting layer; and

Fig. 9 describes the structural formula of aluminium chelate (Alq), used in the electron injection layer.

Referring now to Figure 1, the colour filter includes a transparent substrate 1, colour resolution layers 2 on the transparent substrate 1, a protection layer 4 covering the transparent substrate 1 and the colour resolution layers 2, and a transparent electrode 3 on the protection layer 4. The colour resolution layers 2 contain a red pigment or a red dye, a green pigment or a green dye and a blue pigment or a blue dye. Figure 2 is a cross section of a colour filter, including colour conversion layers and used for the colour conversion according to another embodiment of the invention. Referring now to Figure 2, the colour filter includes colour conversion layers 2 in place of the colour resolution layers of Figure 1. Figure 3 is a cross section showing the substrate and the colour conversion layers of the colour filter of Figure 2. Figure 4 is a cross section of an organic polychromatic-light emitting display device that includes a laminate of an organic EL light emitting element on the colour filter of Figure 2. Referring now to Figure 4, the laminate of the organic EL light emitting element (hereinafter simply referred to as the "organic EL laminate") 5 includes a hole injection layer, a hole transport layer on the hole injection layer, an organic light emitting layer on the hole transport layer, and an electron injection layer on the organic light emitting layer. A cathode 6 is on the organic EL laminate 5. It is not always necessary to dispose the passivation film 7 between the transparent electrode 3 and the protection layer 4, when the protection layer 4 is strong enough chemically and physically to work as a passivation film. The patterned colour resolution layer in Figure 1 is a filter layer that adjusts the colour purity of the light emitted from the organic light emitting layer. The patterned colour conversion layer in

Figure 2 is a fluorescent layer that absorbs the light emitted from the organic light emitting layer and emits fluorescent light. The patterned colour resolution layer and the patterned colour conversion layer are sometimes referred to collectively as the "patterned colour layer" or simply as "colour layer".

A protection layer 4 is formed such that the protection layer 4 covers colour layers 2 arranged on a transparent substrate 1. The colour layers 2 contain respective pigments or dyes. The protection layer 4 is formed in the following way. At first, a film of a mixture containing a polymerizing component (a) and a metal-containing compound (b) is deposited by the wet method. Then, the mixture is polymerized by the cross-linking polymerization reaction using radiation (ultraviolet or visible light), heat, or radiation and heat. The polymerizing component (a) contains monomers, oligomers and/or polymers, capable of being polymerized by radiation, heat, or radiation and heat. The monomers, oligomers and polymers have hydroxyl groups, carboxyl groups or amino groups. The monomers, oligomers and polymers can be polymerized by radiation (ultraviolet or visible light), heat, or radiation and heat. The metal-containing compound (b) is metal alkoxide, metal phenoxide, metal acylate or metal chelate having from 1 to 18 carbon atoms. The protection layer 4 is preferably 15  $\mu\text{m}$  in thickness, and, more preferably, from 1 to 13  $\mu\text{m}$  in thickness to obviate the foregoing problems.

The monomers, oligomers and polymers, which can be polymerized by radiation, heat, or radiation and heat, are soluble to the solvents (typically water or alcoholic solvents) which do not erode the colour layers 2, especially the colour conversion layers, due to their hydrophilic hydroxyl groups, carboxyl groups or amino groups. The soluble monomers, oligomers and polymers facilitate forming a film. The metal-containing compound (b) is soluble to the above described solvents and cross-links with the functional groups of the component (a) by dealcoholation condensation or by forming hydrogen bonds with the hydroxyl groups, carboxyl groups or amino groups. At first, the component (a) and the metal-containing compound (b) are mixed. Then, the reactive terminal groups, preferably acryloyl groups or methacryloyl groups, of the monomers, oligomers and polymers of the component (a) are involved in the subsequent thermal polymerization reaction. It is preferable to make the

reactive terminal groups react with each other at first photochemically. Then, the component (a) is cross-linked by the metal-containing compound (b) between 80 and 160°C, more preferably between 85 and 150°C, and most preferably between 90 and 130°C. By using the two-step process, the quality and the adhesiveness of the protection layer with the substrate 1 and the colour layers 2 are further improved.

Thus, by additionally employing the cross-linking based on the dealcoholation condensation reaction between the functional groups (hydroxyl groups, carboxyl groups or amino groups) and metal-containing compound (b) (metal alkoxide, metal phenoxide, metal acrylate and metal chelate), an excellent protection layer that does not erode the colour layers and exhibits excellent protective properties such as optical resistance, chemical resistance, physical resistance, mechanical resistance and resistance against subsequent manufacturing steps is obtained.

The monomer component that has hydroxyl groups, carboxyl groups or amino groups includes the ester polymers of polyhydric alcohol and acrylic acid and the ester polymers of polyhydric alcohol and methacrylic acid such as vinyl alcohol, acrylic acid, methacrylic acid, hydroxyethyl acrylate, N,N-dimethylaminoethyl acrylate, ethylene glycol acrylate, poly(ethylene glycol acrylate), ethylene glycol methacrylate and poly(ethylene glycol methacrylate); the ester polymers of fumarates; the ester polymers of maleates; and the epoxy resins of bisphenol A type or novolak type.

Some examples of the compounds which have acrylate groups or methacrylate groups at its ends and active functional groups, and can be polymerized by radiation, heat, or radiation and heat, are listed below.

Compounds with one functional group

- 2-hydroxyethyl acrylate
- 2-hydroxyethyl methacrylate
- 2-hydroxyethylacryloyl phosphate
- $\epsilon$ -caprolactam-~~2~~-hydroxyethyl acrylate
- poly(caprolactam acrylate)
- N,N-dimethylaminoethyl acrylate
- N,N-dimethylaminoisopropylacrylamide
- N,N-dimethylacrylamide

Commercial products: ARONIX Series M-5300, M-5400, M-5600,  
M5700 (supplied from TOAGOSEI CO., LTD.)

Compounds with two functional groups

poly (urethane diacrylate)

Commercial Product: ARONIX M-215

(supplied from TOAGOSEI CO., LTD.)

bisphenol A-epichlorohydrin type epoxy diacrylate

pentaerythritol diacrylate monostearate

alicyclic epoxy diacrylate

ethylene glycol diglycidylether diacrylate

ethylene glycol diglycidylether dimethacrylate

poly(propylene glycol diglycidylether diacrylate)

diglycidyl phthalate diacrylate

polybutadiene epoxy addition product containing  
terminal hydrogen groups

bisphenol A-type epoxy diacrylate

Polymers of epoxy diacrylate and brominated epoxy diacrylate of  
bisphenol A-type and novolak type

(RIPOXY Series supplied from Showa Highpolymer Co., Ltd.)

Compounds with three or more functional groups

pentaerythritol acrylate

trimethylolpropane

triacrylate of propylene oxide addition product

pentaerythritol pentacrylate

glycerol polyglycidyl ether polyacrtlate

Commercial products: KAYARAD PET-30, KARAYAD PET-1040  
(supplied from NIPPON KAYAKU CO., LTD.)

Commercial product: BEAMSET EM-90

(supplied from Arakawa Chemical Industries, LTD.)

These compounds are used alone or in the form of a mixture.  
Generally, mixture films exhibit better film properties. These compounds  
may be used with other monomers and oligomers. Polymerization products or

copolymerization products of these compounds may be used as the monomers and oligomers which have reactive terminal groups.

As described earlier, the conventional polar monomers of radiation polymerization type dissolve the pigments in the colour layers. In contrast, the monomers, oligomers and polymers according to the invention, into which the functional groups such as hydroxyl group, carboxyl group and amino group are introduced, do not adversely affect chemically the pigments in the colour layers.

In addition, cation-polymerization-type epoxy compounds having hydroxyl groups and cation-polymerization-type thiol compounds having hydroxyl groups are used effectively as the component (a) that polymerizes by radiation, heat, or radiation and heat.

Preferably, the polymerizing component (a) contains from 10 to 80 weight %, more preferably from 20 to 70 weight %, of the monomers, oligomers and/or polymers having hydroxyl groups, carboxyl groups or amino groups.

The monomers, oligomers and/or polymers in the polymerizing component (a), having the foregoing functional groups, are easily soluble to water and alcoholic solvents which do not dissolve the pigments in the colour layers and facilitate coating a film exhibiting excellent quality. However, when the concentration of the monomers, oligomers and/or polymers in the polymerizing component (a) is more than 80 weight %, many of the hydrophilic functional groups are excessive. Even when the excessive functional groups are used for polymerization, residual functional groups still remain. The residual functional groups cause a highly hydrophilic protection layer and impair the resistive properties of the protection layer. When the concentration of the monomers, oligomers and/or polymers in the polymerizing component (a) is less than 10 weight %, the solubility of the polymerizing component (a) to the solvents that do not affect the pigments in the colour layers is extremely low and the density of the cross-links with the metal-containing compound (b) is also low. Thus, as far as the concentration of the monomers, oligomers and/or polymers in the polymerizing component (a) is less than 10 weight %, the expected protective properties are not obtained even when the polymerizing component (a) is used in combination with the metal-containing compound (b).



Now the metal-containing compound (b) including metal alkoxide, metal phenoxide, metal acylate or metal chelate will be explained.

Al, Ti, Si, Zr, In, Zn, Ni and Cu are used as a central metal. These metals easily produce respective alkoxides, phenoxides, acylates or chelates. These metal-containing compounds condense with the component (a) through ester exchange with water or the group, typically the hydroxyl group, carboxyl group and amino group, having an active hydrogen atom, resulting in cross-linking. Especially, the metal alkoxide conducts very vigorous hydrolysis. The hydrolysis reaction proceeds more slowly as the number of carbon in the substituted alkyl group and aryl group is larger. The hydrolysis speed changes in the order of tert- > sec- > n-. Usually, the reaction speed of phenoxide is not lower than that of alkoxide. The reaction speed is controlled by producing chelate compounds of diketone and keto ester such as ethyl acetoacetate, acetyl acetone and diethyl malonate. Although the alkoxides, phenoxides acylates and chelates of all the metals described above are suitable for the cross-linking agent of the polymerizing component (a), alkoxides and phenoxides of Ti, Al, Zr and Cu having from 2 to 6 carbon atoms are preferable. The complex compounds of metal alkoxide and metal phenoxide are also useful.

Chelate compounds such as di-i-propoxy-titanium-bis(acetyl acetate), di-i-propoxy-silicon-bis(acetyl acetate), di-i-propoxy-zirconium-bis(acetyl acetate), di-n-butoxy-titanium-bis(ethyl acetoacetate) and di-n-butoxy-indium-bis(ethyl acetoacetate) are used.

For initiating the polymerization of the monomer, oligomer and/or polymer having terminal reactive groups, especially acryloyl groups or methacryloyl groups, and polymerized by radiation, heat, or radiation and heat, direct excitation that uses light and indirect excitation that uses a polymerization initiator to produce free radicals are employable. Although both methods are effective, the indirect excitation that uses a polymerization initiator provides with a more stable protection layer. The polymerization initiators of decomposition-type represented by the carbonyl compounds, hydrogen extraction type, ring opening type and ion type are used. These polymerization initiators are used with a reaction promoter to improve the reactivity. The polymerization initiator and reaction promoter are appropriately combined to control the reactivity or to avoid adverse effects of the foregoing radical species to the pigments.

It has been found that it is effective to add 5 weight % or less of the polymerization initiator to the polymerizing component (a).

Some commercially available polymerization initiators are listed below.

Irgacure-184, Irgacure-651, Irgacure-1173, Irgacure-500,

Irgacure-1000, Irgacure-907, Irgacure-369 and Irgacure-1700

(supplied from Ciba-Geigy Japan Limited)

CTX, DETX-S, BP-100, BMS, 2-EAQ and DMBI

(supplied from NIPPON KAYAKU CO., LTD.)

SEKUOL Z, SEKUOL BZ, SEKUOL BEE, SEKUOL BIP

and SEKUOL BI (supplied from SEIKO CHEMICAL CO., LTD.)

The employable initiators are not limited to those listed above, and many combinations may be useful.

Preferably, from 1 to 100 weight parts, more preferably, from 10 to 95 weight parts, of the metal containing compound (b) is used with respect to 100 weight parts of the monomers, oligomers and/or polymer of the invention. When the rate of the metal alkoxide compound is too high, cracks are caused on the colour layers. When the rate of the metal alkoxide compound is too low, the cross-linking density lowers, causing poor resistive properties of the protection layer.

The solvents used for coating the mixed composition of the polymerizing component (a) and the metal-containing compound (b) are water and alcoholic solvents such as ethanol, isopropyl alcohol, n-butanol, isobutanol and their mixtures which do not dissolve the pigments. The concentration of the mixture composition in the solvent is adjusted to obtain the desired film thickness and flatness. Spin-coating, roll-coating and dipping are used alone or in an appropriate combination for coating the solution of the mixed composition to obtain a very flat protection layer.

By irradiating radiation such as an electron beam, ultraviolet light and visible light, by thermo-setting or by the combination of radiation and heat, the polymerizing component (a) is polymerized at first through its terminal groups, preferably acryloyl groups or methacryloyl groups. The most preferable curing method uses the irradiation of ultraviolet light, the irradiation intensity of which is controlled. Then, the functional groups (hydroxyl groups, carboxyl groups or amino

groups) of the polymerizing component (a) and the metal-containing compound (b) are cross-linked in an appropriate temperature range.

The protection layer 4 is preferably 15  $\mu\text{m}$  or less in thickness, and more preferably, from 1 to 13  $\mu\text{m}$  in thickness. Preferably, the protection layer 4 is flat enough such that the concave and convex portions on its surface are 0.2  $\mu\text{m}$  or less in height. Preferably, the protection layer 4 is transparent. Preferably, the glass transition temperature of the protection layer 4 is 140°C or higher. As a result, an excellent hybrid protection layer including an organic-inorganic composite material is obtained. The hybrid protection layer exhibits excellent chemical resistance, physical resistance and mechanical hardness (4H or harder in the pencil hardness designations), and works as a gas barrier.

An ultraviolet light absorber, levelling agent and such ingredients may be added to the protection layer of the invention. A passivation film of 300 nm or thinner may be formed on the protection layer by sputtering  $\text{SiO}_2$ ,  $\text{SiO}$ ,  $\text{Al}_2\text{O}_3$  and such inorganic materials which are not influential optically. Finally, a high-quality colour filter, that can be used practically with no problem, is obtained by forming a transparent electrode 3 on the protection layer of the invention.

Especially, the protection layer used in the colour conversion filter, that includes colour conversion layers, prevents the organic EL element from being deteriorated by the gases evaporating from the colour conversion layers and blocks the organic solvents. In forming the organic EL element (including an anode, an organic layer laminate and a cathode), the protection layer according to the invention protects the materials of the colour filter from low-molecular-weight compounds such as water and monomers, blocks water, oxygen, monomers and such low-molecular-weight components produced from the colour filter by aging or by heat generated by driving the organic EL element, and facilitates driving the organic EL element on the protection layer of the colour filter stably for a long period of time.

Thus, an excellent polychromatic-light emitting display device is obtained according to the invention. The polychromatic-light emitting display device of the invention facilitates maintaining the colour conversion function of the colour filter, flattens the steps between the

colour layers by a coupling layer with the minimum thickness, causes little damage in forming the organic EL element and exhibits a wide angle of visibility.

The materials for the protection layer are not limited to those disclosed herein. Any materials, which can be formed into a film, exhibit a transparency of 50% or more in the wavelength range between 400 and 700 nm, and is resistant against heat generated by the subsequent manufacturing steps and by driving the organic EL element, may be used.

The colour conversion filter shown in Figure 2 includes a planar arrangement of the red pigment layer, green pigment layer and blue pigment layer on the glass substrate 1. Any specific limitations do not exist in forming the colour layers (colour resolution layers in Figure 1 and colour conversion layers in Figure 2). For example, the photolithographic method, the micelle electrolysis method and the screen printing method are used.

Now the present invention will be described in connection with the preferred embodiments and comparative examples.

Although an indium oxide compound (ITO) is used for the anode, copper phthalocyanine (CuPc), 4,4'-bis[N-(1-naphthyl)-N-phenylamino]-biphenyl ( $\alpha$ -NPD), 4,4'-bis(2,2-diphenylvinyl)biphenyl (DPVBi) and aluminium chelate (Alq) in the organic EL laminate in the following embodiments and comparative examples, the materials for the organic EL layer laminate are not limited to those described above.

A blue filter material (Color Mosaic CB-7001 supplied from FUJIFILM OLIN CO., LTD.) is coated by spin coating on a transparent glass substrate and the coated filter material layer is patterned by the photolithographic method, resulting in a patterned blue conversion layer. The pattern of the resulting blue conversion layer consists of stripes, 5  $\mu$ m in thickness and 0.1mm in width, extending in parallel with a pitch of 0.33mm. Then, a negative photoresist soluble to alkali, into which Coumarin 6 (supplied from Aldrich Chemical Co., Inc.) is dispersed is coated by spin coating on the substrate. The coated photoresist is patterned by the photolithographic method and heated at 150°C, resulting in a patterned green conversion layer. The pattern of the resulting green conversion layer consists of stripes, 10  $\mu$ m in thickness and 0.1mm in width, extending in parallel with a pitch of 0.33mm. Then, a negative

photoresist soluble to alkali, into which Rhodamine 6G (supplied from Aldrich Chemical Co., Inc.) is dispersed is coated by spin coating on the substrate. The coated photoresist is patterned by the photolithographic method and heated at 120°C, resulting in a patterned red conversion layer. The pattern of the resulting red conversion layer consists of stripes, 15  $\mu\text{m}$  in thickness and 0.1mm in width, extending in parallel with a pitch of 0.33mm.

The coating liquid for the protection layer according to the first embodiment contains the following components.

glycerol poly(glycidil ether) polyacrylate (DENACOL DA-314 supplied from Nagase Chemicals Ltd.)	... 30 weight %
1,3-bis[2(acryloyloxy)ethyl]-5-hydroxy ethyl isocyanurate (ARONIX M-215 supplied from TOAGOSEI CO., LTD.)	... 15 weight %
neopentylglycol diacrylate	... 5 weight %
2-hydro-2-phenoxypropyl acrylate (ARONIX M-5700 supplied from TOAGOSEI CO., LTD.)	... 7 weight %
Initiator: Irgacure 1174 (supplied from Ciba-Geigy Japan Limited)	... 1.8 weight %
SEIKUOL BBI (supplied from SEIKO CHEMICAL CO., LTD.)	... 1.2 weight %
titanium tetra-n-butoxide (TBT supplied from Nippon Soda Co. Ltd.)	... 40 weight %

The above described photo-polymerizing polymer derivative composition (consisting of the above components) is diluted by a mixed solvent consisting of 65 weight parts of isopropyl alcohol and 35 weight parts of water such that the solution contains 60 weight % of solid components. The solution is coated by spin coating on the foregoing colour conversion layers. The polymer derivative composition is cured by irradiating light from a high pressure mercury lamp with energy intensity of 500 mJ/cm<sup>2</sup> and by drying in an oven at 100°C for 30 min., resulting in a protection layer.

Then, an ITO transparent electrode 3 is formed by sputtering to obtain a colour filter. Then, an organic EL laminate is formed in the following way to obtain a polychromatic-light emitting device.

An organic EI laminate consisting of five layers (hole injection layer/hole transport layer/light emitting layer/electron injection layer/cathode) as shown in Figure 4 is formed on the colour filter formed as described above.

At first, a transparent electrode (ITO) layer is formed on the entire upper surface of the protection layer formed, as shown in Figure 2, on the colour layers. The ITO layer is patterned by coating a photoresist agent (OFPR-800 supplied from Tokyo Ohka Kogyo Co., Ltd.), by positioning a mask for obtaining a line pattern consisting of stripes 0.096 mm in width and extending in parallel with a pitch of 0.11 mm such that the mask position is adjusted with the pattern of the colour conversion layers below, by irradiating light (365 nm) with energy intensity of 200 mJ/cm<sup>2</sup> and by developing the line pattern with developing liquid (NMD-3 supplied from Tokyo Ohka Kogyo Co., Ltd.).

Then, the substrate with the layers laminated so far is loaded in a resistance-heating vacuum deposition chamber and a hole injection layer, a hole transport layer, a light emitting layer and an electron injection layer are deposited one by one without braking the vacuum. During the film deposition, the vacuum chamber is evacuated to  $1 \times 10^{-4}$  Pa.

Copper phthalocyanine (CuPc), the structural formula of which is described in Figure 6, is deposited, resulting in a hole injection layer. The resulting hole injection layer is 100 nm in thickness.

Then, 4,4'-bis[N-(1-naphthyl)-N-phenylamino]-biphenyl ( $\alpha$ -NPD), the structural formula of which is described in Figure 7, is deposited, resulting in a hole transport layer. The resulting hole transport layer is 20 nm in thickness.

Then, 4,4'-bis(2,2-diphenylvinyl)biphenyl (DPVBi), the structural formula of which is described in Figure 8, is deposited, resulting in a light emitting layer. The resulting light emitting layer is 30 nm in thickness.

Then, aluminium chelate (Alq), the structural formula of which is described in Figure 9, is deposited, resulting in an electron injection layer. The resulting electron injection layer is 20 nm in thickness.

Then, the substrate with the layers laminated so far is taken out from the vacuum deposition chamber and loaded again in a resistance-heating vacuum deposition chamber. Mg/Ag (10:1 in weight

ratio) is deposited, resulting in a cathode extending in perpendicular to the anode. The resulting cathode is 200 nm in thickness.

The mixed polymer composition for the protection layer according to the second embodiment contains 40 weight % of a di-n-butoxy-bis(triethanol aminate) titanium compound (TAT supplied from Nippon Soda Co., Ltd.) in substitution for 40 weight % of titanium tetra-n-butoxide (TBT). The mixed polymer composition is diluted with the solvent according to the first embodiment. The diluted mixed polymer composition is coated on the colour layers formed in the same manner as in the first embodiment and cured, resulting in a protection layer. The resulting protection layer covering the colour layers is treated in the same manner as in the first embodiment, resulting in a colour conversion filter. A polychromatic-light emitting device according to the second embodiment is fabricated using the resulting colour conversion filter in the same manner as in the first embodiment.

The coating liquid for the protection layer according to the third embodiment contains the following components.

glycerol poly(plycidyl ether) polyacrylate (DENACOL DA-314  
supplied from Nagase Chemicals Ltd.) ... 35 weight %  
pentaerythrithol acrylate (ARONIX M-305  
supplied from TOAGOSEI CO., LTD.) ... 10 weight %  
DPHA (KAYARAD DPHA supplied from  
NIPPON KAYAKU CO., LTD.) ... 10 weight %  
2-hydro-2-phenoxypropyl acrylate (ARONIX M-5700  
supplied from TOAGOSEI CO., LTD.) ... 10 weight %  
Initiator: Irgacure 651 (supplied from Ciba-Geigy Japan Limited)  
... 1 weight %  
KAYACURE 2-EQA (supplied from  
NIPPON KAYAKU CO., LTD.) ... 1 weight %  
SEIKUOL BBI (supplied from  
SEIKO CHEMICAL CO., LTD.) ... 1 weight %  
titanium tetra-i-propoxide (TPT supplied from  
Nippon Soda Co. Ltd.) ... 32 weight %

The above described photo-polymerizing polymer derivative composition (consisting of the above components) is diluted by a mixed solvent consisting of 65 weight parts of isopropyl alcohol and 35 weight parts of water such that the solution contains 60 weight % of solid components. The solution is coated by spin coating on the colour conversion layers formed in the same manner as in the first embodiment. The polymer derivative composition is cured by irradiating light from a high pressure mercury lamp with energy intensity of 500 mJ/cm<sup>2</sup> and by drying in an oven at 100°C for 30 min., resulting in a protection layer. The resulting protection layer covering the colour layers is treated in the same manner as in the first embodiment, resulting in a colour conversion filter. A polychromatic-light emitting device according to the third embodiment is fabricated using the resulting colour conversion filter in the same manner as in the first embodiment.

The coating liquid for the protection layer according to the fourth embodiment contains the following components.

1,3-bis[2(acryloyloxy)ethyl]-5-hydroxy ethyl isocyanurate (ARONIX M-215 supplied from TOAGOSEI CO., LTD.) ...	35 weight %
oligoester polyacrylate (ARONIX M-8030 supplied from TOAGOSEI CO., LTD.) ...	15 weight %
epoxy phthalate acrylate (DENACOL DA-721 supplied from Nagase Chemicals Ltd.) ...	10 weight %
Initiator: Irgacure 1174 (supplied from Ciba-Geigy Japan Limited) ...	1 weight %
SEIKUOL BBI (supplied from SEIKOHEMICAL CO., LTD.) ...	1 weight %
KAYACURE 2-EAQ (supplied from NIPPON KAYAKU CO., LTD.) ...	1 weight %
zircon tetra-i-propoxide ...	32 weight %

The above described photo-polymerizing polymer derivative composition (consisting of the above components) is diluted by a mixed solvent consisting of 65 weight parts of isopropyl alcohol and 35 weight parts of water such that the solution contains 60 weight % of solid components. The solution is coated by spin coating on the colour conversion layers formed in the same manner as in the first embodiment.



The polymer derivative composition is cured by irradiating light from a high pressure mercury lamp with energy intensity of 500 mJ/cm<sup>2</sup> and by drying in an oven at 120°C for 30 min., resulting in a protection layer. The resulting protection layer covering the colour layers is treated in the same manner as in the first embodiment, resulting in a colour conversion filter. A polychromatic-light emitting device according to the fourth embodiment is fabricated using the resulting colour conversion filter in the same manner as in the first embodiment.

The thermal resistance of the protection layers according to the embodiments represented by their glass transition temperatures is 140°C or higher. The flatness of the protection layers according to the embodiments is such that the heights of the concave and convex portions on the layers are less than 0.2  $\mu$ m. The protection layers according to the embodiments do not erode the line pattern of the colour layers.

The protection layer according to the comparative example 1 is formed by spin-coating a hard coating agent (KAYARAD M-010 supplied from NIPPON KAYAKU CO., LTD.) including ultraviolet-curing multifunctional acrylate oligomers on the colour layers, by irradiating light (365 nm) with energy intensity of 500 mJ/cm<sup>2</sup> and by baking at 80°C.

Then, a transparent electrode is formed on the protection layer in the same way as in the first embodiment, resulting in a colour filter. Then, an organic EL element including an anode, an organic layer laminate and a cathode is formed on the resulting colour filter in the same way as in the first embodiment.

The protection layer according to the comparative example 2 is formed by coating the coating liquid, into which 95 weight parts of a photo-curing multifunctional urethane resin (EM-90 supplied from Arakawa Chemical Industries, LTD.) and 5 weight parts of a polymerization initiator (Irgacure 184 supplied from Ciba Specialty Chemicals K. K.) are dissolved, by irradiating light (365 nm) with energy intensity of 1500 mJ/cm<sup>2</sup> and by heating at 80°C.

Then, a transparent electrode is formed on the protection layer in the same way as in the first embodiment, resulting in a colour filter. Then, an organic EL element including an anode, an organic layer laminate and a cathode is formed on the resulting colour filter in the same way as in the first embodiment.

The protection layer according to the comparative example 3 is formed by coating a thermo-setting protecting agent (HP-1009 supplied from Hitachi Chemical Co., Ltd.), including two-liquid-type epoxy resin that has been used to obtain a highly flat and transparent protection film, under the spin-coating condition of 700rpm/10 sec. and by drying the coated layer in an oven by preheating at 80°C for 2 min. and at 100°C for 2 min., followed by baking at 200°C for 1 hour.

Then, a transparent electrode is formed on the protection layer in the same way as in the first embodiment, resulting in a colour filter. Then, an organic EL element including an anode, an organic layer laminate and a cathode is formed on the resulting colour filter in the same way as in the first embodiment.

The protection layer according to the comparative example 4 is formed by spin-coating a composite inorganic coating agent (supplied from Nissan Chemical Industries, Ltd.) including  $\text{SiO}_2$  as its main component, by drying the coated layer at 80°C for 5 min. and by baking the dried layer at 150°C for 1 hour.

Then, a transparent electrode is formed on the protection layer in the same way as in the first embodiment, resulting in a colour filter. Then, an organic EL element including an anode, an organic layer laminate and a cathode is formed on the resulting colour filter in the same way as in the first embodiment.

The devices E1 through E4 (according to the first through fourth embodiments) and the devices C1 through C4 (according to the comparative examples 1 through 4) are evaluated. The results are listed in Table 1. The evaluation method for each term and its result will be explained later.

Table 1

	Thickness of the protection layers ( $\mu\text{m}$ )	Flatness	Open circuits in the ITO electrode	Pencil hardness	Peeling	Life of the device	Influences to the pigments
E1	10	$< \pm 0.2 \mu\text{m}$	Not caused	6H	Excellent	Long	Not caused
E2	10	$< \pm 0.2 \mu\text{m}$	Not caused	5H	Excellent	Long	Not caused
E2	10	$< \pm 0.2 \mu\text{m}$	Not caused	5H	Excellent	Long	Not caused
E4	10	$< \pm 0.2 \mu\text{m}$	Not caused	5H	Excellent	Long	Not caused
C1	11	$< \pm 0.2 \mu\text{m}$	Not caused	5H	Poor	Short	Caused
C2	10	$< \pm 0.2 \mu\text{m}$	Not caused	4H	Poor	Medium	Tolerable
C3	10	$< \pm 0.2 \mu\text{m}$	Not caused	4H	Excellent	Short	Caused
C4	1	$> \pm 8 \mu\text{m}$	Caused	5H	Excellent	Long	Not caused

The thickness of the protection layer is defined as the height between the surface of the transparent substrate and the upper surface of the protection layer. As described in Table 1, the protection layers according to the embodiments of the present invention are around 10  $\mu\text{m}$  in thickness, that is thick enough to protect the pigments.

The steps (concave and convex portions) caused in the protection layer surfaces are evaluated by a surface roughness meter (DEKTAK IIA supplied from ULVAC JAPAN Ltd.). The height of the steps (concave and convex portions) caused in the surfaces of the protection layers according to the invention distributes within  $\pm 0.2 \mu\text{m}$  indicating that the protection layers according to the invention are sufficiently flat. Neither open circuits nor short circuits are observed in the transparent electrodes of the colour filters according to the invention.

When an inorganic coating agent is used according the comparative example 4, the protection layer is 1  $\mu\text{m}$  in thickness, too thin to flatten the steps between the colour conversion layers, leaving unburied steps of higher than  $\pm 8 \mu\text{m}$ . Open circuits and short circuits are caused in the transparent electrode above the step surfaces. Therefore, the protection layer according to the comparative example 4 is not suitable to practical use.

Pencil hardness of the protection layers are measured by the "Pencil hardness test" according to the Japanese Industrial Standards (JIS). It has been found that the hardness of the protection layers according to the embodiments is 5H or harder in the pencil hardness designations.

The adhesiveness of the protection layer formed on a glass substrate is evaluated by the crosshatch test that counts the caused peelings of 1 mm X 1 mm as defined by JIS (Japanese Industrial Standards) K 6301. The protection layers which earn 9 points or more are classified into the excellent class. The protection layers according to the present invention exhibit excellent adhesiveness.

Figure 5 is a set of curves plotting the dark spot sizes in the display devices E1 through E3 according to the first through third embodiments and display device C2 according to the comparative example 2. The display devices are placed in a nitrogen gas stream and growth of dark spots in a light emitting area (2mm X 2mm) is observed under an optical microscope. It has been confirmed that the protection layers according to the invention interrupt the hazardous components such as water and monomers, originally contained in the fluorescent materials and the binder matrices for the fluorescent materials or produced from the fluorescent materials and the binder matrices by the heat generated during driving the display device, which deteriorate the organic El element and prevent dark spots from growing.

The influences of the protection layers are evaluated on the basis of the changes in the CIE chromaticity coordinate caused when the display devices E1 through E4 according to the first through fourth embodiments and the comparative display devices C1 through C4, placed in a nitrogen gas stream, emit monochromatic light. It has been confirmed that the fluorescent materials protected by the protection layers according to the invention work stably after the organic El element is formed.

As explained above, the colour filter according to the invention meets all the following requirements that its protection layer is the one (i) that neither erodes the pattern of the colour layers nor deactivates the fluorescent materials in the colour layers, (ii) that is thick enough to bury the steps between the colour layers but thin enough (several  $\mu\text{m}$ ) to provide a wide angle of visibility; (iii) that is highly transparent

optically, (iv) that exhibits excellent thermal resistance, (v) that has flat and smooth surface, (vi) that exhibits excellent adhesiveness to the colour layers and the substrate, (vii) that exhibits excellent chemical resistance, (viii) that is highly moisture proof, (ix) that does not cause evaporation of residual monomers and solvent from it, (x) that is mechanically strong to some extent, (xi) that has no protrusions of foreign materials on its surface, and (xii) that endures the subsequent manufacturing steps. Thus, the protection layer according to the invention enables to manufacture an organic polychromatic-light emitting display device easily with low manufacturing costs. The organic polychromatic-light emitting display device, including the protection layer according to the invention, converts the light from its light emitting element to polychromatic light with high luminance very efficiently and stably for a long period of time.

### Claims

1. A colour filter comprising:
  - a transparent substrate;
  - patterned colour layers on the transparent substrate, each of the patterned colour layers being formed by patterning a resin film containing a pigment;
  - a transparent and flat protection layer covering the transparent substrate and the patterned colour layers; and
  - a transparent electrode on the protection layer;
  - the protection layer comprising a cross-linking polymerization product of a mixture containing a polymerizing component (a) and a metal-containing compound (b), the mixture being deposited by the wet method such that a layer of the mixture is formed, the cross-linking polymerization using radiation, heat, or radiation and heat;
  - the polymerizing component (a) comprising monomers, oligomers or polymers, capable of being polymerized by radiation, heat, or radiation and heat;
  - the monomers, oligomers and polymers having hydroxyl groups, carboxyl groups or amino groups;
  - the metal-containing compound (b) being alkoxide, phenoxide, acylate or chelate of a metal atom having from 1 to 18 carbon atoms.
2. The colour filter according to Claim 1, wherein the monomers, oligomers or polymers have acryloyl groups or methacryloyl groups and the metal atom is the one selected from the group consisting of Al, Zr, Si, In, Zn, Ni, Ti, and Cu.
3. The colour filter according to Claim 1, wherein the protection layer contains from 1 to 100 weight parts of the metal-containing compound (b) with respect to 100 weight parts of the monomers, oligomers or polymers.
4. The colour filter according to Claim 1, wherein the glass transition temperature of the protection layer is 140°C or higher, the thickness of the protection layer is 15 $\mu$ m or thinner, and the concave and convex portions on the surface thereof are 0.2  $\mu$ m or less in height.
5. The colour filter according to Claim 1, wherein at least one or two of the pigments exhibit a colour conversion function.

6. An organic polychromatic-light emitting display device comprising:

a colour filter; and

an organic electroluminescent element on the colour filter, the organic electroluminescent element comprising an organic light emitting layer, the organic light emitting layer emitting light by carrier injection;

the colour filter comprising a transparent substrate, patterned colour layers on the transparent substrate, each of the patterned colour layers being formed by patterning a resin film containing a pigment, a transparent and flat protection layer covering the transparent substrate and the patterned colour layers, and a transparent electrode on the protection layer;

the protection layer comprising a cross-linking polymerization product of a mixture containing a polymerizing component (a) and a metal-containing compound (b), the mixture being deposited by the wet method such that a layer of the mixture is formed, the cross-linking polymerization using radiation, heat, or radiation and heat;

the polymerizing component (a) comprising monomers, oligomers or polymers, capable of being polymerized by radiation, heat, or radiation and heat;

the monomers, oligomers and polymers having hydroxyl groups, carboxyl groups or amino groups;

the metal-containing compound (b) being alkoxide, phenoxide, acylate or chelate of a metal atom having from 1 to 18 carbon atoms;

the colour filter emitting polychromatic light in response to the light from the organic light emitting layer.

7. The organic polychromatic-light emitting display device according to Claim 6, wherein the monomers, oligomers or polymers have acryloyl groups or methacryloyl groups and the metal atom is the one selected from the group consisting of Al, Zr, Si, In, Zn, Ni, Ti, and Cu.

8. The organic polychromatic-light emitting display device according to Claim 6, wherein the protection layer contains from 1 to 100 weight parts of the metal-containing compound (b) with respect to 100 weight parts of the monomers, oligomers or polymers.

9. The organic polychromatic-light emitting display device according to Claim 6, wherein the glass transition temperature of the protection layer is 140°C or higher, the thickness of the protection layer is  $1 \mu\text{m}$  or thinner, and the concave and convex portions on the surface thereof are  $0.2 \mu\text{m}$  or less in height.
10. The organic polychromatic-light emitting display device according to Claim 6, wherein at least one or two of the pigments exhibit a colour conversion function.





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Claims searched: 1-10

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**Patents Act 1977**  
**Search Report under Section 17**

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.R): C3P (PKN)

Int Cl (Ed.7): G02B(5/20, 5/22, 5/23, 5/24, 5/26, 5/28)

Other: ONLINE: EPODOC, JAPIO, WPI.

**Documents considered to be relevant:**

Category	Identity of document and relevant passage	Relevant to claims
X	WPI Abstract Accession No. 1989-202315 [28] & JP 11040186 A (EPSON), see Abstract.	1, 2 at least.

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.